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Systematic computation of phase partition and solubilities in phase transfer catalytic processes

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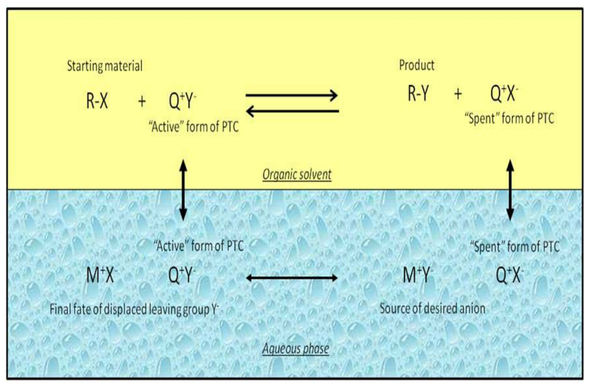
Abstract

Phase transfer catalysis (PTC) is a general methodology applicable to a great variety of reactions in which inorganic anions react with organic compounds. In PTC, reactions are performed in heterogeneous two phase systems in which there is a negligible mutual solubility of the phases. One aqueous phase serves as a reservoir of reacting anions, whereas organic reactants are located in a second, organic phase. The key feature of this approach is the use of a catalytic amount of an organic soluble cation (often a quaternary ammonium cation) to induce solubilization of the reactive anion in the organic phase while trying to minimize the partition of the product anion. Therefore the determination of the solubility and the related equilibrium partitioning of the active and inactive form of the PT catalyst between the two phases is critical for the design of successful phase transfer catalytic processes.

1. Introduction

PTC mechanism



- Synthesis of organic molecules from two reactants located in immiscible phases (one organic phase and one aqueous phase)
- A phase transfer catalyst added to transfer one reactant from its normal phase into a different phase where it encounters the second reactant

Process insights

- Mutual solubility between organic solvent and water
- PTCs present in different aggregation status in the:
  - organic phase: PTCs dissociate into ions
  - aqueous phase: PTCs present as ion pairs
- The active and the spent form of the catalyst distribute between the organic and the aqueous phase ➡ The ratio between the active and the spent form of the catalyst in the organic phase determines the extent of conversion of the organic reaction

⬇

Solubility model based calculations and partition between phases are critical for the development of PTC processes

2. Solubility calculations framework

A. Decomposition into 4 binary systems

A. Organic solvent - water
B. Inorganic salt - water
C. Organic solvent - PTC
D. PTC – water

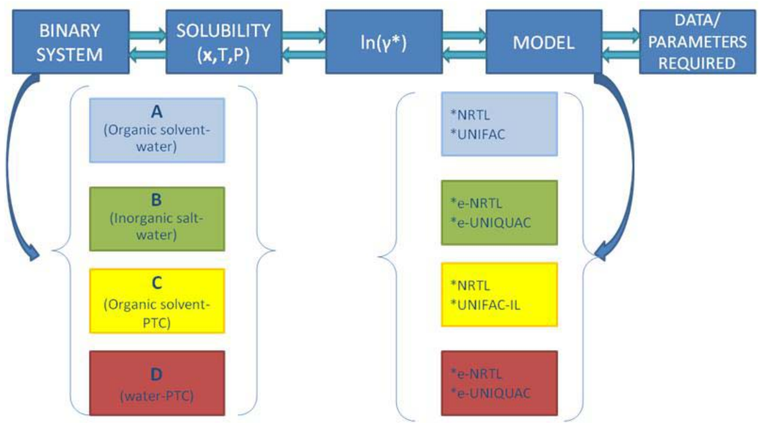
B. Collection of experimental solubility data

Binary System	Number of systems studied	Number of data points
A (Organic solvent-water) LLE data	9	494
B (Inorganic salt-water) - SLE data - Experimental mean activity coefficient data	10	271
C (Organic solvent-PTC) SLE data	172	251
D (water-PTC) - SLE data - Experimental mean activity coefficient data	43	89

C. Development+identification of the model for each binary subsystem:

- model for mixture γ^{LLE} and γ^{SLE} are needed
- parameters of constitutive models for γ calculations are needed

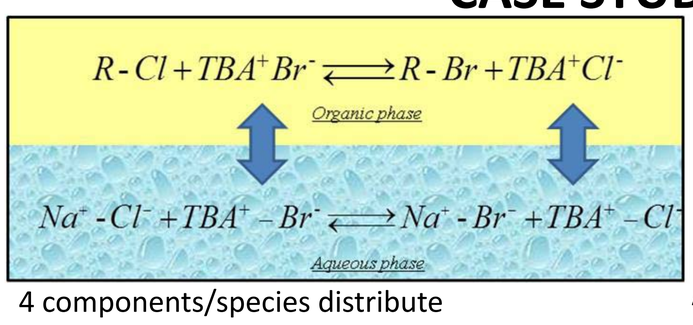
Constitutive models



Equilibrium models

A (Organic solvent-water) LLE	$x_i^{org}\gamma_i^{org} = x_i^{aq}\gamma_i^{aq}$
B (Inorganic salt-water) SLE	$x_i\gamma_i = \exp\left(\frac{\Delta H_f}{RT_m}\left(1-\frac{T_m}{T}\right)+A+B\frac{1}{T}\right)$
C (Organic solvent-PTC) SLE	$x_i\gamma_i = \exp\left(\frac{\Delta H_f}{RT_m}\left(1-\frac{T_m}{T}\right)+\frac{\Delta H_{tr,1}}{RT_{tr,1}}\left(1-\frac{T_{tr,1}}{T}\right)+\frac{\Delta H_{tr,2}}{RT_{tr,2}}\left(1-\frac{T_{tr,2}}{T}\right)+\frac{\Delta C_{p,m}}{R}\left(\ln\frac{T}{T_m}+\frac{T_m}{T}-1\right)\right)$
D (water-PTC) SLE	$x_i\gamma_i = \exp\left(\frac{\Delta H_f}{RT_m}\left(1-\frac{T_m}{T}\right)+\frac{\Delta H_{tr,1}}{RT_{tr,1}}\left(1-\frac{T_{tr,1}}{T}\right)+\frac{\Delta H_{tr,2}}{RT_{tr,2}}\left(1-\frac{T_{tr,2}}{T}\right)+\frac{\Delta C_{p,m}}{R}\left(\ln\frac{T}{T_m}+\frac{T_m}{T}-1\right)\right)$

3. Application of the methodology to an industrial CASE STUDY



Production of benzyl bromide

R - Cl = Benzyl Chloride
R - Br = Benzyl Bromide
TBA^+Br^- = Active catalyst
TBA^+Cl^- = Inactive catalyst
organic solvent = Toluene

4 components/species distribute (are in equilibrium) between the two phases: toluene, water, active and inactive catalysts ➡ An equilibrium relation can be written for each of them

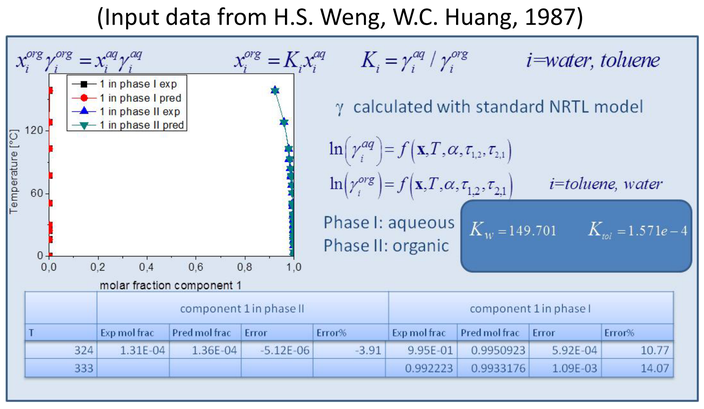
$x_i^I\gamma_i^I = x_i^{II}\gamma_i^{II}$ or $x_i^I = K_i x_i^{II}$

with K_i: partition coefficient

Example of calculations:

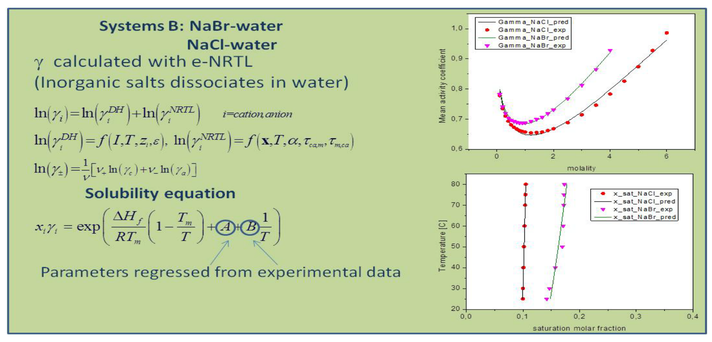
(Input data from H.S. Weng, W.C. Huang, 1987)

System A: Toluene-water



T	component 1 in phase II: Exp mol frac	Pred mol frac	Error	Error%	component 1 in phase I: Exp mol frac	Pred mol frac	Error	Error%
324	1.31E-04	1.36E-04	-5.12E-06	-3.91	9.95E-01	0.9950923	5.92E-04	10.77
333					0.992223	0.9933176	1.09E-03	14.07

System B: NaCl-water, NaBr-water



Active and inactive PTC partition beween water and organic phases

$x_{TBABr}^{org}\gamma_{TBABr}^{org} = x_{TBA+}^{aq}x_{Br-}^{aq}\gamma_{TBABr\pm}^{aq}$ $x_{TBABr}^{org} = K_{TBABr}x_{TBA+}^{aq}x_{Br-}^{aq}$ $K_{TBABr} = \frac{\gamma_{TBABr\pm}^{aq}}{\gamma_{TBABr}^{org}}$

$x_{TBACl}^{org}\gamma_{TBACl}^{org} = x_{TBA+}^{aq}x_{Cl-}^{aq}\gamma_{TBACl\pm}^{aq}$ $x_{TBACl}^{org} = K_{TBACl}x_{TBA+}^{aq}x_{Cl-}^{aq}$ $K_{TBACl} = \frac{\gamma_{TBACl\pm}^{aq}}{\gamma_{TBACl}^{org}}$

System C: TBABr-toluene, TBACl-toluene

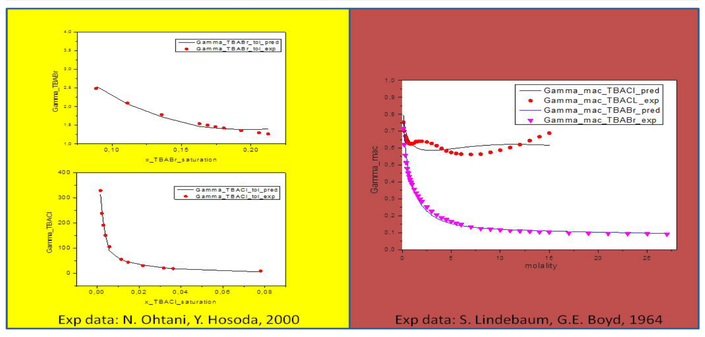
1. Experimental data points are available for this system ⬇ NRTL parameters fitted
   $\ln(\gamma_{TBABr}^{org}) = f(\mathbf{x},T,\alpha,\tau_{TBABr,tol},\tau_{tol,TBABr})$
   $\ln(\gamma_{TBACl}^{org}) = f(\mathbf{x},T,\alpha,\tau_{TBACl,tol},\tau_{tol,TBACl})$
2. γ also calculated with UNIFAC-IL (new cation and anion groups defined) Necessary approach to tackle lack of exp data pointed out for other systems
   $\ln(\gamma_i) = \ln(\gamma_i^C) + \ln(\gamma_i^R)$
   $\ln(\gamma_i^C) = f(\mathbf{x},R_k,Q_k)$, $\ln(\gamma_i^R) = f(\mathbf{x},Q_k,T,a_{m,k})$

γ calculated with e-NRTL (PTC dissociates in water)

$\ln(\gamma_i) = \ln(\gamma_i^{DH}) + \ln(\gamma_i^{NRTL})$ i=cation,anion
$\ln(\gamma_i^{DH}) = f(I,T,z,\varepsilon)$, $\ln(\gamma_i^{NRTL}) = f(\mathbf{x},T,\alpha,\tau_{ca,m},\tau_{m,ca})$
$\ln(\gamma_\pm) = \frac{1}{\nu}[\nu_+\ln(\gamma_+) + \nu_-\ln(\gamma_-)]$

$K_{TBABr} = 7.279e-3$ $K_{TBACl} = 1.366e-3$

System D: TBABr-water, TBACl-water



4. Conclusions

A reliable thermodynamic framework for the calculation of solubilities and phase partition in phase transfer catalytic processes has been developed and illustrated through an industrial case study:

- The system has been decomposed into binary subsystems
- The appropriate thermodynamic models have been developed/selected for each subsystem
- A database of solubility data has been built and used to regressed parameters model and validate the modelling approach
- The partition coefficient of the component/species which distribute between the two phases has been readily calculated

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